Reducing Interfacial Resistance in Garnet-Structured Solid-State Lithium-Ion Batteries

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Abstract

While the development of conventional lithium-ion (Li-ion) batteries has reached mature stage, a number of battery researchers are already looking forward to replace the liquid electrolytes in conventional lithium-ion batteries to solid-state electrolyte due to its improved safety and larger volumetric energy density. Among the various solid electrolyte materials, inorganic $Li_{6.75}La_3Zr_{1.75}Ta_{0.25}O_{12}$ (LLZTO) compound with garnet phase has drawn significant attention due to its stability in contact with metallic Li. However, the most critical challenge in achieving a high-performance solid-state battery with LLZTO electrolytes is the high interfacial resistance between the electrolyte and electrode materials. In this study, I synthesized LLZTO powder. Then dense LLZTO electrolyte pellets will be made by using sintering method. During the sintering process, I continuously adjusted the sintering temperature to increase the relative density of the LLZTO pellets. Finally, the bulk conductivity of sintered LLZTO pellets was measured by electrochemical impedance spectroscopy (EIS) technique.

Introduction

Compared with conventional lithium-ion batteries, solid-state batteries have obvious advantages. Solid-state batteries have better safety due to the use of solid-state electrolytes (SSEs) instead of liquid electrolytes in traditional lithium-ion batteries. Solid-State batteries are non-flammable, non-corrosive, and free of liquid leakage. Due to the good mechanical strength of SSEs, solid-state batteries can have higher energy densities while preventing internal short-circuiting by the penetration of Li dendritic Solid-State batteries could have 2 times energy than traditional batteries for the same volume. Furthermore, solid-state electrolytes can achieve higher volumetric energy density by minimizing battery packaging [1]. However, until now, the development of high-performance solid-state batteries has not met expectations whose major challenge is large interfacial resistance between electrolyte and electrode materials due to the nature of solid-solid contact [2]. Many experimental teams have adopted different methods to try to solve this problem. For example, the one-step soldering technique to quickly coat molten li onto the solid-state electrolyte surface or using the atomic layer deposition method to coat ZnO on the SSE surface to reduce the interfacial resistance between electrolyte and electrode materials, but the effect did not meet expectations[3-4,11]. Usually, the lithium-ion conductivity of liquid electrolytes measures 10^{-2} S cm^{-1}, but there is no solid electrolyte that can achieve this conductivity. One of the best performing solid-state electrolyte material known so far is $Li_{6.75}La_3Zr_{1.75}Ta_{0.25}O_{12}$ (LLZTO), which is garnet-type structure metal oxide. Since it has relatively high electrical conductivity, wide electrolytic window (up to 6 Volts), and good stability to lithium metal it is considered as a promising candidate for SSE. [3] However, LLZTO's lithium-ion bulk conductivity is only 10^{-4} to 10^{-3} S cm^{-1}, and the interfacial and

intragrain conductivities are even as low as 10^{-6} S cm^{-1} [3,4], which is much smaller than that of liquid electrolyte. This is because Li-ions transfer through contact between particles, and the contact between the particles in the solid electrolyte cannot be as close as the liquid electrolyte [1-4]. Therefore, high-temperature sintering is required to improve ionic conductivity in SSE pellets. Under the action of high temperature, contact mode between the particles change from point contact to surface contact due to the grain growth, and the contact area is greatly increased. However, it is very important to find a suitable condition for SSE sintering. When the sintering temperature is too low or sintering time is to short, the grain would not grow enough to make good contact, which will cause relatively low relative density and poor conductivity. When the sintering temperature is too high or sintering time is too long, lithium evaporation may occur which will result in low Li-ionic conductivity.[8] Therefore, LLZTO electrodes can only achieve high performance under the proper sintering temperature and sintering time.

The experimental objective of this research is to develop a recipe to control the relative densities of LLZTO electrolytes from 50% to 90%. Sintering temperature will be modified for porosity control. After sintering, the conductivities of LLZTO electrolytes will be measured. This research will provide key information for the future solid-state device manufacture.

Methodology

Synthesize of LLZTO Powder

The first step of this research is to prepare LLZTO powder. LLZTO powder is determined to be synthesized by using solid-state reaction method based on V. Thangadurai's work. [5-7] Based on the chemical equation of LLZTO, which is $Li_{6.75}La_3Zr_{1.75}Ta_{0.25}O_{12}$, the molar mass of LLZTO is calculated to be 860.3343 g/mol. Each experiment requires approximately 0.02 molar LLZTO powder. Based on the molar mass of LLZTO and number of molars that needed for experiment, the total mass of LLZTO powder is calculated to be 17.2067g. The total mass of LLZTO powder is used as a reference to calculate the mass that needed of $LiCO_3$, ZrO_2, Ta_2O_5, and La_2O_6 powders for each trail of experiment by using molar mass of each powder times ratio number and number of molar. The stoichiometric amounts of Li_2CO_3, ZrO_2, Ta_2O_5, and La_2O_3 are calculated to be 6.4847 g, 4.3129g, 1.1047g and 9.7746g, respectively. Mixing the stoichiometric amounts of $LiCO_3$, ZrO_2, Ta_2O_5, and La_2O_6 powders to obtain LLZTO powder that will be used for each trail of experiment.

Fabrication of dense LLZTO solid electrolyte pellets

For this step, sintering treatment is applied on the obtain LLZTO powder. Obtained powder from the last step will be ground for 24 hours by using ball mill machine. Zirconia balls is added into powders to help ground them. Zirconia balls will not have any chemical reaction with LLZTO powder. At the same time, the continuous friction between the Zirconia balls and the powder particles can ensure that the particles of the LLZTO powder are ground to the small size. Filter the Zirconia balls and get the ground LLZTO powder. Obtained powder will be

heating at 900 ºC for 12 hours. This step can ensure that excess oxygen and carbon are evaporated in the form of gas, leaving the LLZTO ($Li_{6.75}La_3Zr_{1.75}Ta_{0.25}O_{12}$) powder required for the experiment. At the same time, excessive $LiOH{\cdot}H_2O$ (10 wt %) will be added to heated LLZTO powders to compensate for the loss of lithium during the heating processes. Obtained LLZTO powders will be reground for 24 hours by using ball mill machine with Zirconia balls to require size. And using scanning electron microscopy (SEM) to observe the resulting powder to make sure all LLZTO powder particles are ground to a size of 10 to 100 nanometers, shown in Figure 1.

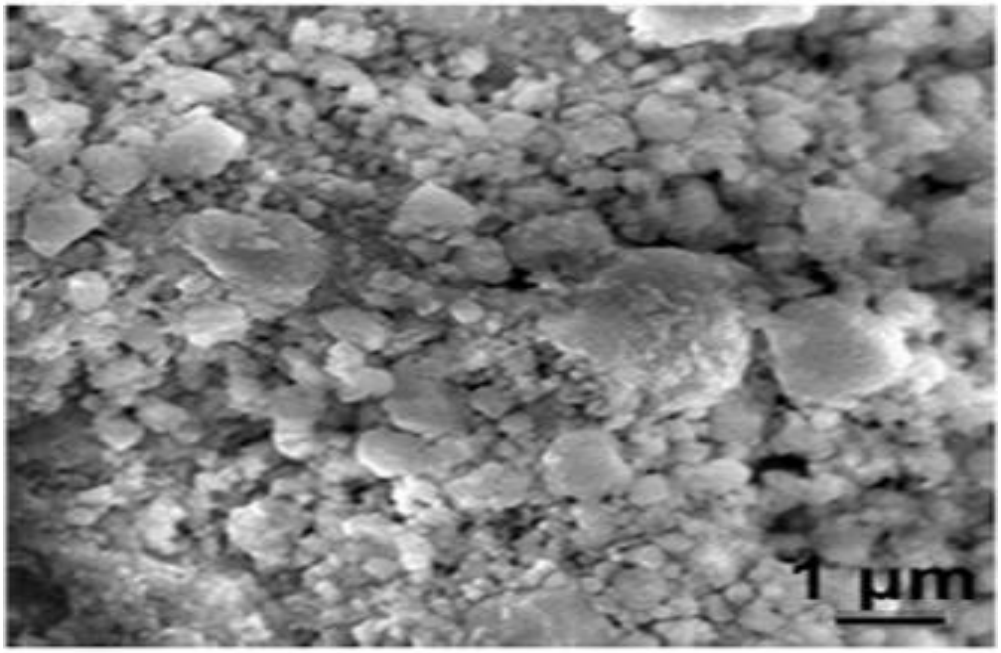

Figure 1: Using scanning electron microscopy (SEM) to observe the LLZTO powder [1].

After the ball milling, LLZTO powders have already met the experimental particle size requirements, so every 0.75 g of powder will be taken out and dry pressed into LLZTO pellet under the pressure of 3 tons using by using the Dry Pressing Die. Sintering treatment will be applied to result LLZTO pellets. The LLZTO pellets will be heated around 1200 ºC for 3 hours

with 2 ^{o}C/min ramping by using high temperature muffle furnace. Dense LLZTO solid electrolyte pellets are fabricated by using high temperature sintering to increase the relative density of LLZTO pellets.

EIS Performance Analysis

EIS analysis will be applied to dense LLZTO pellets to evaluate the separate electronic and ionic components of the total charge transport in LLZTO solid-state electrolytes. EIS involves the employment and proper interpretation of low amplitude variable frequency AC measurements. EIS is a technique that often called as impedance spectroscopy. [9] Before the EIS, the LLZTO pellets after sintering need to be polished to ensure that each pellet has a smooth surface. This is to ensure that EIS only measures the bulk impedance of the pellets. Place the polished pellets in the sputter coating tool and coat the surface of the pellets with Pd-Au alloy. Finally, connect the pellets after the coating to AC current, and draw the impedance spectroscopy of LLZTO pellets by Waveform generator. The conductivity of LLZTO pellet itself will be obtained by analyzing the impedance spectrum drawn.

Discussion

In this research, the most critical step is to increase the relative density of LLZTO electrolytes to improve the conductivity of LLZTO. This research applied sintering process to achieve this aim. Sintering happens naturally in Garnet-Structured materials, such as LLZTO pellets. In a high-temperature environment, this temperature is usually lower than the melting point of the material, the atoms in the Garnet-Structured materials diffuse across the boundaries of the particles and fuse the particles together and creating solid pieces inside the materials. At the same time, sintering can change the arrangement of particles in LLZTO materials, so that the particles are changed from point connection to surface connection. Therefore, the contact area of particles inside LLZTO will be greatly increased, providing more channels for electrons and Li ions. According to the physical properties of LLZTO materials, 1180 °C -1200 °C is considered to be a good sintering temperature window. Therefore, the initial experiment chooses to conduct in the temperature range of 1180 to 1200°C. Using 5 °C as an interval, the LLZTO pellets were sintered at 1180°C, 1185°C, 1190°C, 1195°C, and 1200°C using the high temperature muffle furnace with 2 °C/min ramping, and keep heat the LLZTO pellets at the target temperature for 3 hours. Calculate the density of LLZTO pellets by measuring the volume and mass of LLZTO pellets after sintering and calculate the relative density by comparing LLZTO pellet densities with the theoretical density value of LLZTO materials, which is 5.246 g/cm^3. The experiment results are shown in Table 1.

Table 1: Relative density of LLZTO pellets at 1180-1200 °C range.

Temperature (°C)	1180	1185	1190	1195	1200
Mass (g)	0.6710	0.6319	0.6431	0.6653	_
Diameter (cm)	1.365	1.297	1.254	1.214	_
Thickness (cm)	0.172	0.169	0.166	0.159	_
Density (g/cm^3)	2.666	2.830	3.146	3.615	_
Relative Density	50.82%	53.95%	59.97%	68.91%	_

Plot the results in Table 1 as following:

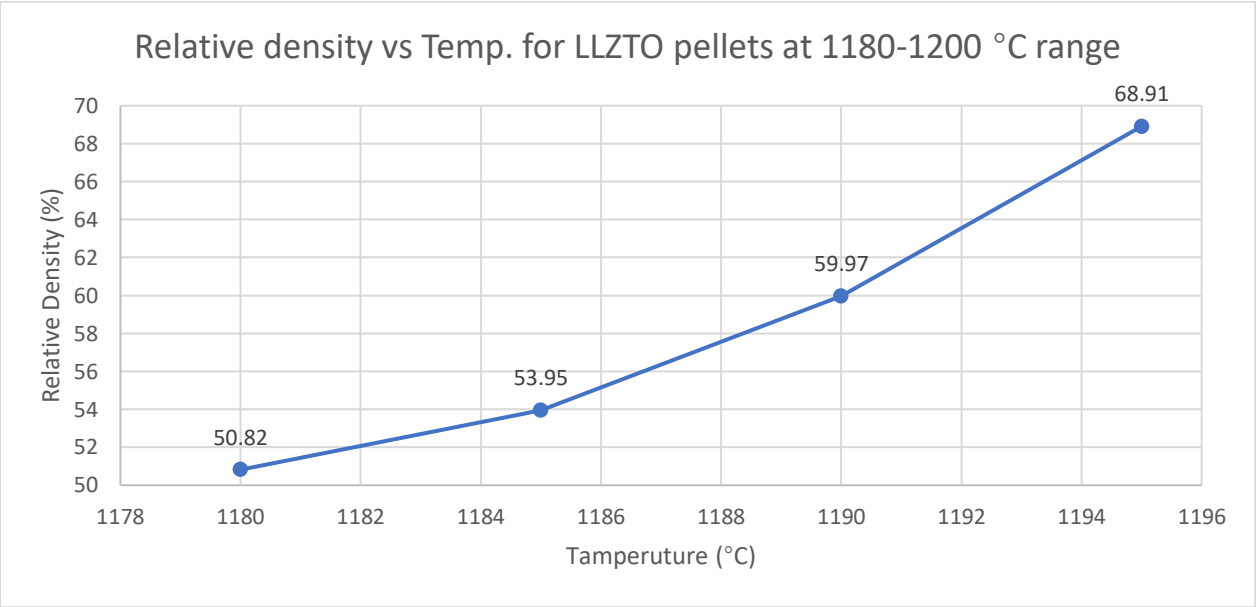

Figure 2: Relative density vs. temperature curve for LLZTO pellets at 1180-1200 °C range.

Based on the results from Table 1 and Figure 2, When the temperature of sintering increased from 1180 ° C to 1195 ° C, the relative density of LLZTO pellets increased significantly. The relative density increased from 50.82% to 68.91%. The effect of sintering temperature on LLZTO pellets is very obvious. As shown in the trend in Figure 2, the relative density of LLZTO pellets increases with increasing temperature in the selected interval. However, when the research tried to be sintering the LLZTO pellets at 1200 °C for 3 hours, the phenomenon of melting frequently occurs in LLZTO pellets after sintering. LLZTO pellets meltdown and stick together after sintering and cause subsequent measurements to be impossible. Melted LLZTO pellets shown in Figure 3.

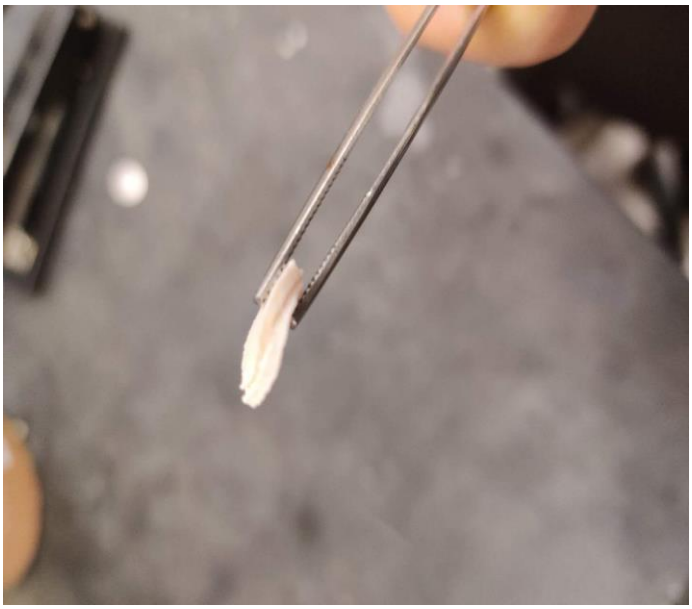

Figure 3: LLZTO pellets melt after sintering at 1200 °C for 3 hours.

Based on the sintering results at 1200 °C, the experiment adopted a new sintering method at 1200°C. The new method grinds LLZTO pellets that fail to be sintered into large particles by hand grinding. These LLZTO particles will be used as bed powder. During each sintering, use bed powder to evenly cover LLZTO pellets. During the sintering process, bed powder can protect LLZTO pellets and allow pellets to be heated evenly, reducing the phenomenon of melting. By using the new sintering method, the research conducted three sets of experiments with 1200 °C as the sintering temperature, and the experimental results are shown in Table 2.

Table 2: Relative density of LLZTO pellets at 1200 °C.

	Trial 1	Trial 2	Trial 3
Mass (g)	0.2168	0.3978	0.3348
Diameter (cm)	0.986	1.024	0.993
Thickness (cm)	0.065	0.121	0.093
Density (g/cm^3)	4.368	3.992	4.649
Relative Density	83.27%	76.01%	88.62%

Plot the results in Table 2 as following:

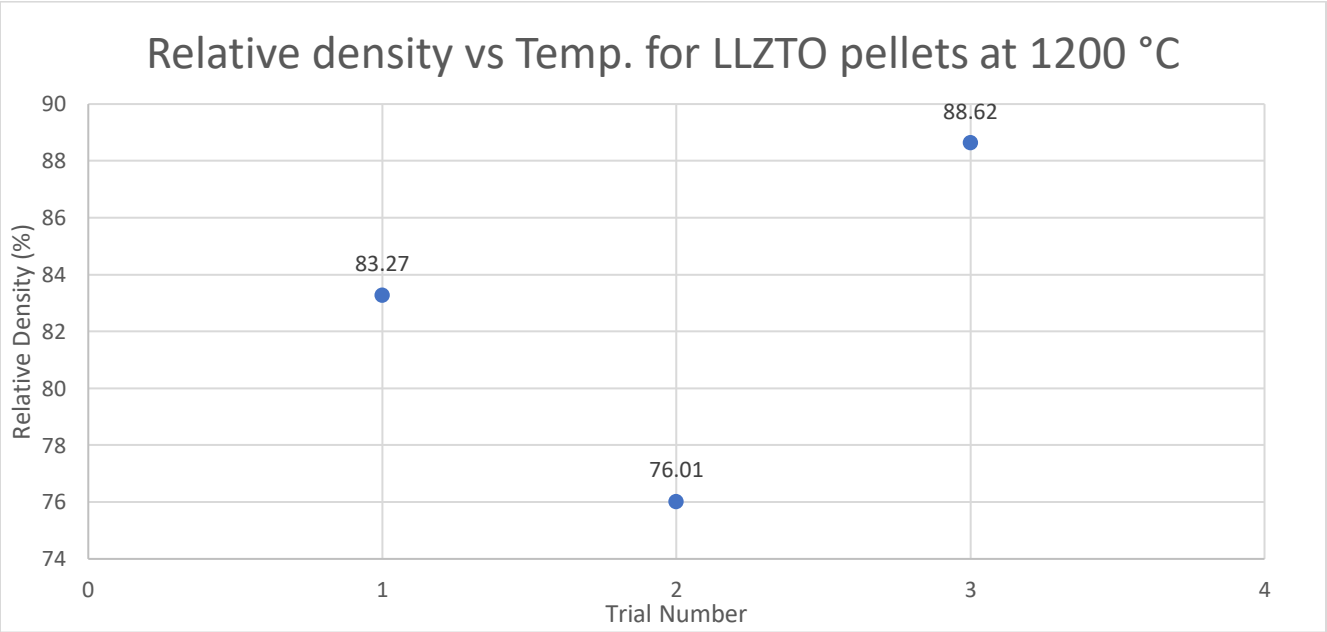

Figure 4: Relative density vs. temperature for LLZTO pellets at 1200 °C.

According to the results shown in Table 2 and Figure 4, using the new method to sinter LLZTO pellets at 1200 °C for 3 hours can greatly increase the relative density of LLZTO pellets, making the relative density of LLZTO pellets at least 75% or more, compared with the result at 1195 °C , the relative density increased by at least 7.1%. In the best experimental situation, the relative density of LLZTO even reached 88.62%.

The idea that high-temperature sintering can significantly increase the relative density of LLZTO pellets is also demonstrated by tracking the variation in the particle size of the same LLZTO pellet at different stages of the sintering experiment. All SEM images were taken for the same LLZTO pellet after sintering at 900 °C. In the Figure 5 and 6, the SEM images were taken after the LLZTO powder was ball milled for 12 and 24 hours, respectely. And finally, the Figure 7 is cross sectional image taken for the LLZTO pellet after sintered at 1210 °C for 3 hours. And the relative density of this LLZTO pellet was measured as 85.90%.

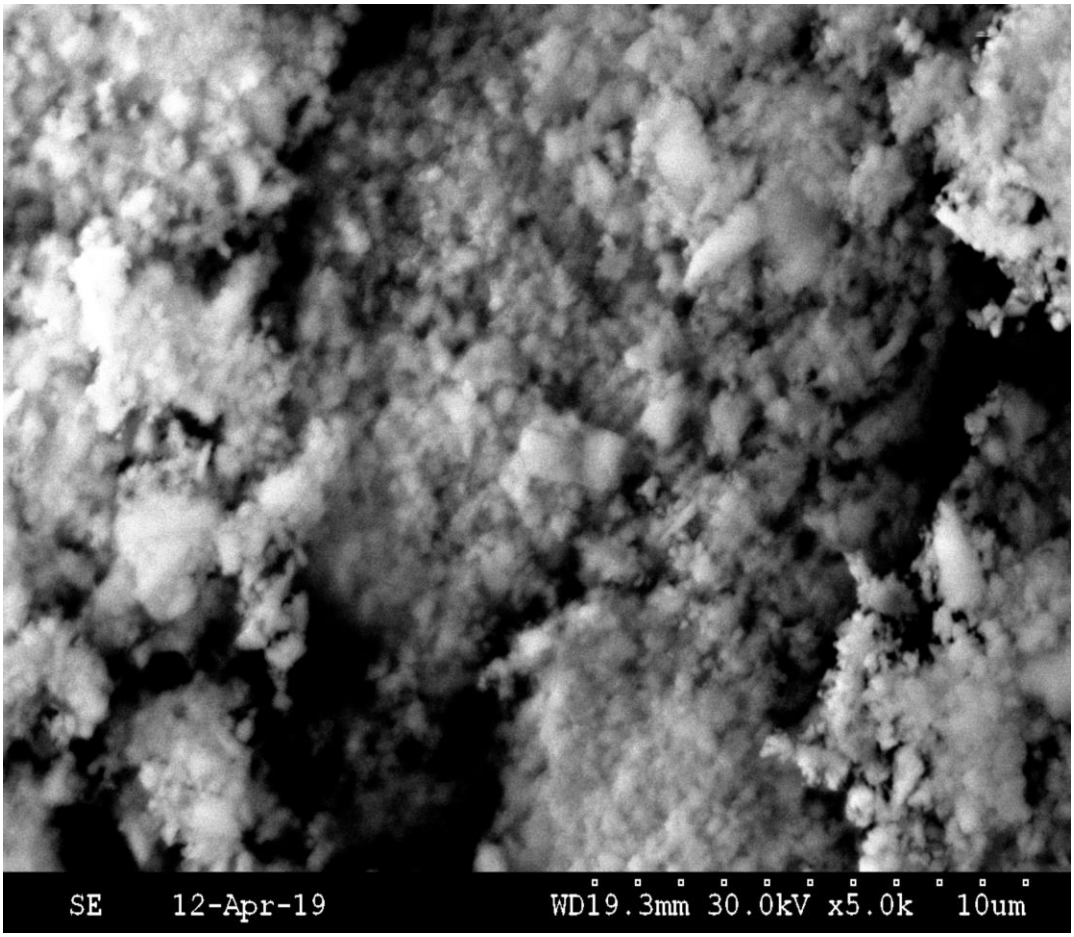

Figure 5: Using SEM to observe LLZTO powder after 12 hours ball milling.

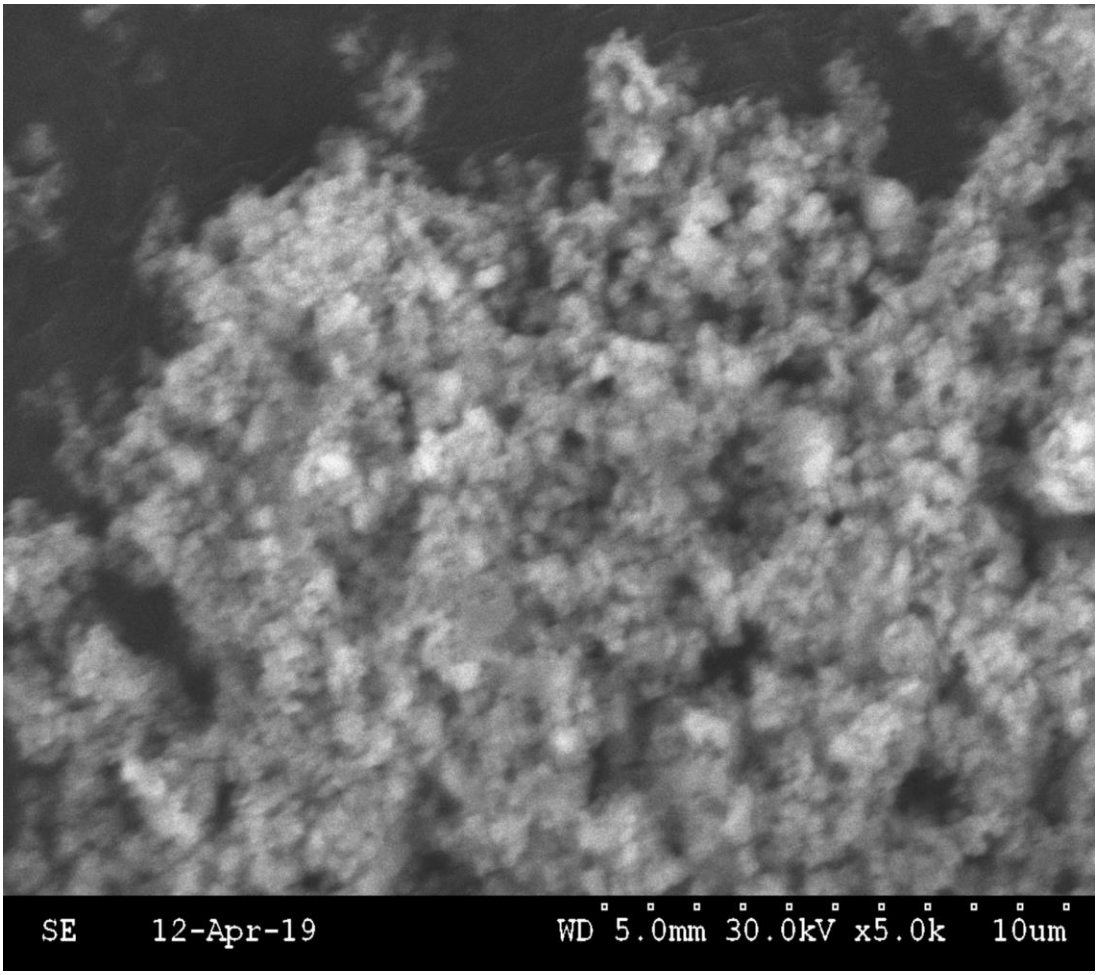

Figure 6: Using SEM to observe LLZTO powder after 24 hours ball milling.

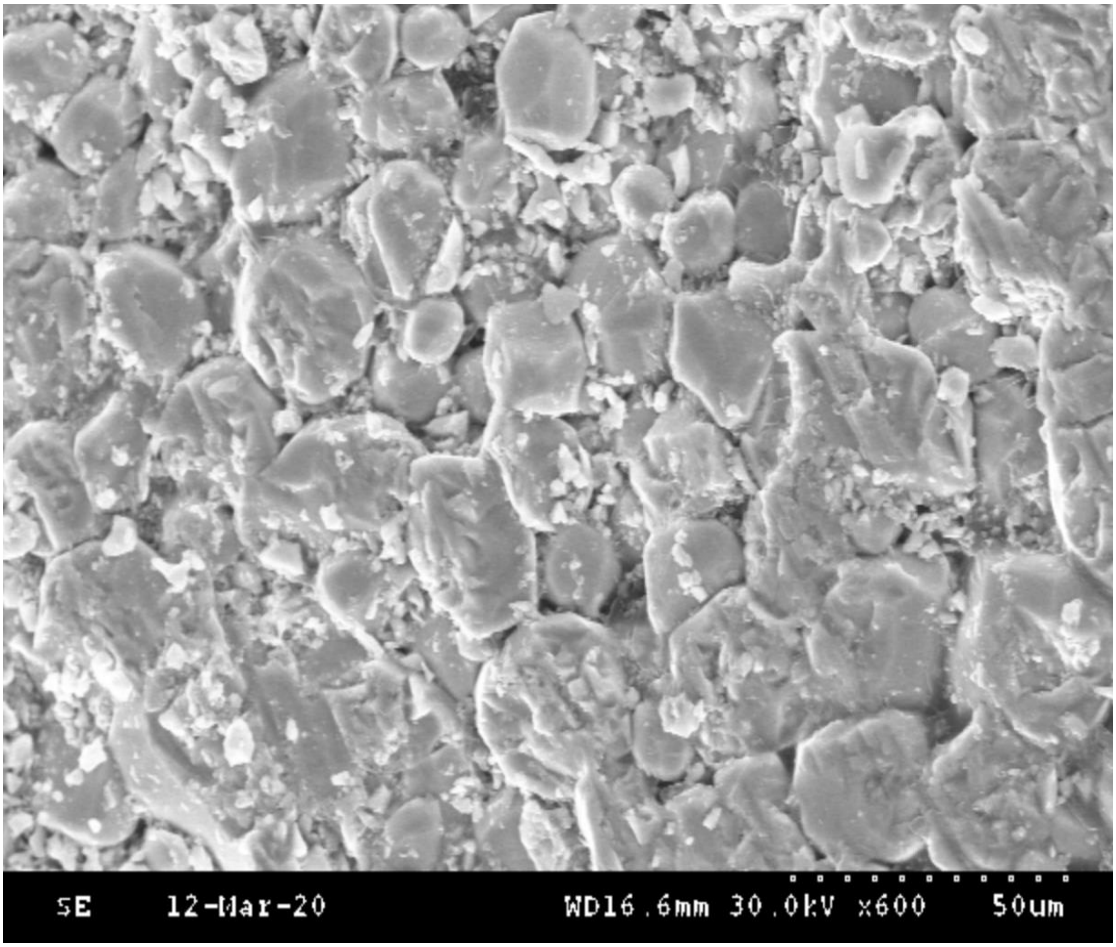

Figure 7: Using SEM to observe LLZTO pellet after sintering at 1210 1210 °C for 3 hours.

Comparing the LLZTO particles from Figure 5 and 6. Which LLZTO powder milled after 12 hours and 24 hours. The powder with 24-hour ball milling has a smaller particle size than a 12-hour grinded powder. The relative density can be improved by physically reducing the particle size of the LLZTO power. But the effect is not very noticeable and due to incomplete intergranular contact, a large number of nonuniform pores are clearly observed from figure 5 and 6. Looking at the results in Figure 7, it is clear to see that the grain boundaries are reduced because of the growth and fusion of the grains due to sintering, and there is a significant increase in the size of the grains while the observable pores are significantly reduced. As a result, its microstructure is denser. Thus, based on the results presented in Figures 5, 6 and 7, it can be

verified that sintering can remarkably promote the grain growth and expel the pores from grain boundaries, leading to density enhancement of LLZTO pellets.

The conductivity of LLZTO pellets also needs to be measured. By sintering at 1210^{o}C for three hours, two pieces of LLZTO particles with a relative density greater than 90% of the theoretical value are obtained. And by conducting EIS analysis on two pieces of LLZTO pellets, the conductivity of LLZTO electrolyte can be obtained through fittings and calculations. Specs of LLZTO pellets are shown in Table 3.

Table 3: Specs of two LLZTO pellets that are conducting EIS analysis.

	Pellets 1	Pellets 2
Mass (g)	0.2997	0.3283
Diameter (cm)	0.975	0.971
Thickness (cm)	0.079	0.080
Relative Density	96.86%	105.64%

EIS was performed on two LLZTO pellets with symmetric blocking electrodes with the same condition to determine the ionic conductivity and charge transfer resistance. The raw EIS data were fitted with a series of three parallel combinations of R//CPE circuits, shown in Figure 8.

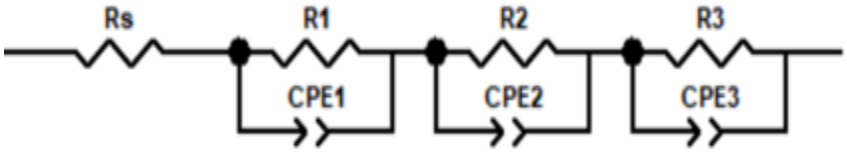

Figure 8: Parallel combination of R//CPE circuits.

In the Circuit, R is corresponding to ohmic resistance and CPE is corresponding to a constant phase element. And an additional resistance is included in the series with circuit to solve the inductive effect. Plot the EIS results by using the Nyquist plot for two LLZTO pellets with both raw and fitted data as following:

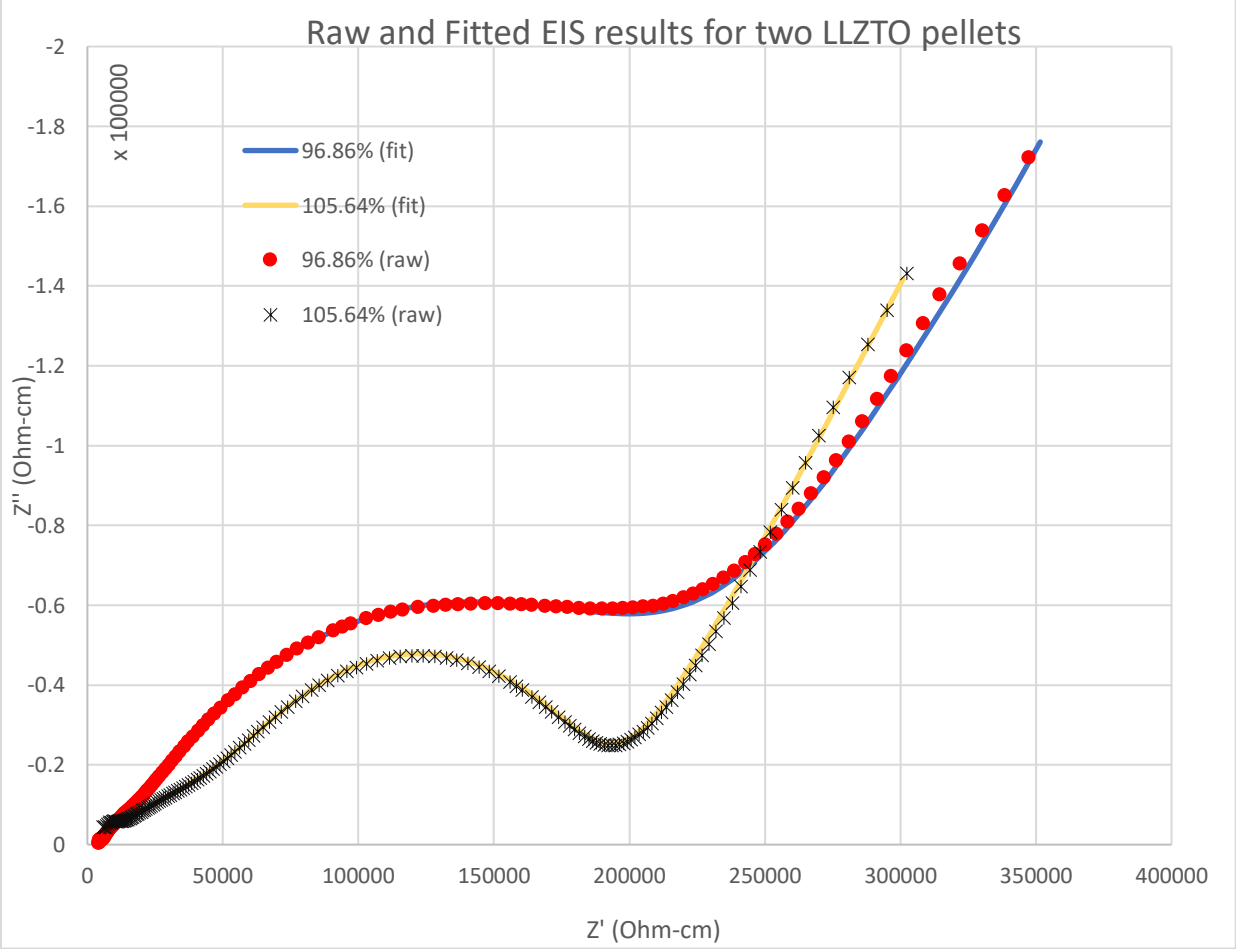

Figure 9: Raw and fit EIS results for the two LLZTO pellets.

Using the fitted data and plot the EIS result for two LLZTO pellets individually. The apparent bulk ionic conductivity and the apparent grain boundary resistance for each pellet can be calculated based on the R//CPE circuit.

For pellet which has 96.86% relative density:

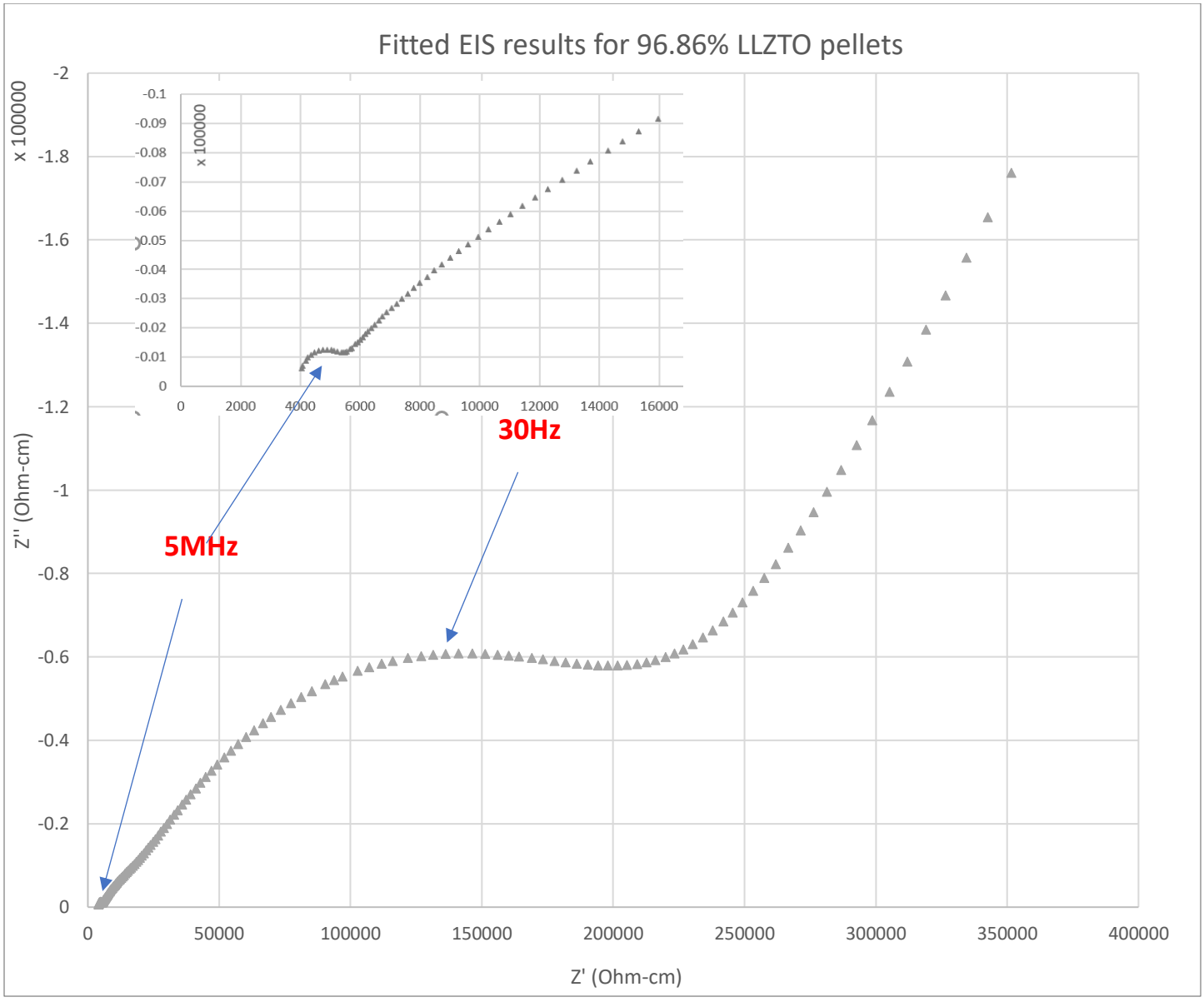

Figure 10: Fit EIS results for the 96.86% LLZTO pellet.

Performance results shown in Table 4:

Table 4: Performance of 96.86% LLZTO pellet.

R1 (Ω-cm)	908.32
σ1 (S/cm)	1.10×10^{-3}
C1 (F)	8.73×10^{-10}
R2 (Ω-cm)	11445.01
σ2 (S/cm)	8.74×10^{-5}
C2 (F)	1.70×10^{-8}
R3 (Ω-cm)	202003.00
σ3 (S/cm)	4.95×10^{-6}
C3 (F)	3.08×10^{-7}

Based on the geometrically corrected capacitance and ionic conductivity values extracted from the fitted EIS plot for the 96.86% LLZTO pellet at high frequency range, which are 8.73×10^{-10} F and 1.10×10^{-3} S/cm, respectively. This relatively low capacitance value is typical for a bulk ion transport. Therefore, the extracted ionic conductivity, σ1, can be attributed to the bulk conductivity of the 96.86% LLZTO pellet. And for the second R//CPE circuit, the capacitance value extracted from fitted EIS plot at intermediate frequency range is 1.70×10^{-8} F. And this capacitance value is determined that will be varied proportionally with the thickness of the same material pellets. Hence, the R2//CPE2 circuit is associated with grain boundary transport. The capacitance extracted from fitted EIS plot for the 96.86% LLZTO pellet at low frequency range is 3.08×10^{-7} F. This is a typical value in the range of electrolyte/electrode interfacial response. Therefore, R3//CPE3 circuit is associated with interfacial charge transfer of

two blocking electrode [10]. Same analysis is applied to pellet which has which has 105.64% relative density.

Figure 11: Fit EIS results for the 105.64% LLZTO pellet.

And extracted R//CPE values from EIS plot in Table 5:

Table 5: Performance of 105.64% LLZTO pellet.

R1 (Ω-cm)	3317.26
σ1 (S/cm)	3.01×10^{-4}
C1 (F)	2.28×10^{-10}
R2 (Ω-cm)	98790.00
σ2 (S/cm)	1.01×10^{-5}
C2 (F)	8.47×10^{-9}
R3 (Ω-cm)	101058.21
σ3 (S/cm)	9.90×10^{-6}
C3 (F)	1.04×10^{-7}

Based on the 2 sample EIS results, $\sigma_{bulk,}$ which is σ1 from Tables 4 and 5, LLZTO pellets that sintered at 1210 ^{o}C for 3 hours is in the range of 3.01×10^{-4}- 1.10×10^{-3} S/cm.

Conclusion and Path Forward

During this research, the sintering strategy was applied for LLZTO pellets. The experimental results showed that at 1200 °C, using bad powder to cover LLZTO pellets and sintering for 3 hours can significantly improve the relative density of LLZTO pellets to 75 % and the above. In this study, it was shown that this sintering method has a huge effect on improving the relative density and conductivity of LLZTO pellets. EIS analysis was also applied on the LLZTO pellets to shown that bulk conductivity for LLZTO pellets sintered in this research is in a range of 3.01×10^{-4}- 1.10×10^{-3} S/cm. Due to time constraints, this research did not complete the study on how does coating process will affect the conductivity of solid-state batteries using LLZTO as electrolyte. After confirming that the sintering method designed in the study can significantly increase the relative density and conductivity of LLZTO pellets, this research will focus on the study about how Al_2O_3 coating will improve the contact between LLZTO pellet and Li metal, and improve the LLZTO solid-state batteries conductive.

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